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COMPLETE SPECIFICATION.

Improvements in or relating to the Coating of Organic Plastic Material with Metal.

We, METAPLAST COMPANY INC., of 244, Fifth Avenue, New York, United States of America, a corporation organised under the laws of the State of New York, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to a process for metallizing organic plastic materials such as for example, phenolic resins, urea and melamine resins, acrylic, styrene, vinyl and cellulose plastics, waxes, rubber or material coated therewith.

It is an object of the invention to provide such a process which is convenient, dependable and comparatively inexpensive.

Another object of the invention is to provide an improved process for treating the surface of an organic plastic material of the above type so that an adherent metal coating may be applied thereto.

Another object is to provide an improved process for applying to the surface of an organic plastic material a conductive layer having characteristics suitable for subsequent electroplating.

A further object is to provide a process of the above type which is adapted to apply the metallic or coated layer in the form of a design.

A further object is to provide a process for stencilling a metallic coating on an organic plastic material.

A still further object is to provide an organic plastic material having a coating of the above type.

Another object is to provide a process of the above type which is particularly suitable for metallizing the surface of cellulose acetate products.

Another object is to provide pre-treating solutions suitable for use in the above process.

Various other objects and advantages will be apparent as the nature of the invention is more fully disclosed.

[*Price* 2/-]

The invention accordingly provides a method of metallizing the surface of an organic plastic material which includes the pre-treatment of the surface of the material for sensitizing said surface preparatory to metallizing with an aqueous solution of stannous chloride including hydrochloric acid in quantity such that the solution becomes clear and remains clear during said treatment.

It is generally well known *per se* that the addition of hydrochloric acid to a solution of stannous chloride prevents precipitation, for example, of the oxychloride.

The solution preferably comprises the following ingredients in the proportions specified :

Stannous Chloride ..	grams 360
Hydrochloric Acid, sp. gr. 1.20	cc. 216
Water	cc. 4000

The invention also provides the method of metallizing the surface of an organic plastic material which comprises treating the surface with the solution as aforesaid of stannous chloride and hydrochloric acid to cause the same to have characteristics suitable for metallizing, washing the surface to remove said solution and applying to said surface a solution of silver nitrate, ammonia and a reducing agent under conditions to precipitate the silver thereon to form a metallic layer.

Viewed from another aspect, the invention provides the method of metallizing the surface of a cellulose ester product which comprises treating said surface with a caustic alkali solution to depolish the same, washing the surface to remove said alkali solution, then treating the depolished surface with the solution of stannous chloride and hydrochloric acid as aforesaid, to cause the same to have characteristics suitable for metallizing, washing the surface to remove said stannous chloride solution and applying to said surface a solution of silver nitrate, ammonia and a reducing agent under

conditions to precipitate the silver thereon to form a metallic layer.

The present process comprises in general so treating the surface of an organic plastic material that an adherent metallic layer may be applied thereto. This layer may be used for subsequent electroplating or, in certain instances, may be polished or otherwise treated to provide the finished surface.

It has been found that organic plastic materials of the type above referred to, and particularly the synthetic plastics, require certain pretreatment before the metallizing operation can be efficiently carried out. This pretreatment may produce a physical or chemical change in the surface itself or may result in the provision of a film of highly reactive material on the surface, although we do not limit ourselves to either of these explanations. Whatever the action of the pretreating material, the step has been found to be essential in order to obtain the subsequent deposition of an adherent metallic layer.

More specifically, the material is first cleaned and then depolished. Usually these two operations can be combined. It is then given the pretreatment hereinafter referred to to condition the same for the metallizing operation. Thereafter, the surface is washed and a suitable silver solution is supplied to deposit silver on the surface as a metallic coating. This coating is sufficiently adherent to be polished or otherwise treated to provide the finished surface or may be used as a conducting layer for the subsequent electroplating of the metallic portion.

As a specific example of one method of carrying out this process, the material, such as a phenol condensation product or other synthetic resin, may first be cleaned and depolished, either by chemical means, such as by the use of a known reagent having the property of depolishing the surface, such as acetone, trichlorethylene or nitric acid or more particularly for styrene plastics, ethylene chlorhydrin; or by mechanical means, such as by sand blasting.

For cellulose acetate and other cellulose ester products, the depolishing may be replaced by the use of a solution of caustic alkali such as sodium or potassium hydroxide. The concentration of this solution should be adjusted to the time and temperature of treatment. Typical conditions are, for solutions of:—

(*a*) Normal alkali, i.e. 40 grams sodium hydroxide per litre:

5 minutes at 80° F. or 10 minutes at 70° F.

(*b*) 2-normal alkali, i.e. 80 grams sodium hydroxide per litre:

5 minutes at 70° F. or 10 minutes at 60° F.

This solution, which we term a priming solution, has the property of conditioning the surface to receive the subsequent treatment.

After the priming or sand blasting, above described, the material is washed of all abrasives or solutions used in the depolishing operation. The depolished, wet material is then subjected to the pretreating or sensitizing solution, which is a solution containing stannous chloride. A water solution containing stannous chloride alone is fairly satisfactory when freshly prepared. However, water solutions of stannous chloride slowly hydrolyse, the stannous ion precipitating as the hydroxide, oxy-chloride or other basic salt. Because of this precipitation, a sensitizing solution comprising stannous chloride in water must be kept agitated during use to keep the stannous chloride suspended, the time of pretreatment may be long, for example, thirty minutes, and the solution soon loses its effectiveness. We have found, however, that the addition of hydrochloric acid to the solution decreases the time required for the pretreatment, and extends the useful life of the sensitizing solution. The hydrochloric acid is used in a quantity such that the solution becomes clear and remains clear under the conditions of use. Such a clear solution is capable of effecting the desired pretreatment in an extremely short time. The material may, for example, be dipped in this solution or the solution may be applied to the surface for a period of fifteen seconds to two minutes. It is understood, of course, that the exact time and concentrations may be varied, the less concentrated solutions requiring the longer times. The concentration of stannous chloride and hydrochloric acid is usually adjusted to the amount of material to be sensitized. During use, the concentration slowly decreases owing to adsorption of the ingredients by the articles being treated. Furthermore, if alkaline solutions were used in an earlier operation, e.g. depolishing, traces of alkali are frequently carried over into the sensitizing solution, where they neutralize some of the hydrochloric acid, eventually causing some precipitation of the stannous chloride. Typical concentration of the sensitizer solution is:

For treatment of a very large amount of material, which was not subjected to alkaline solutions:

Stannous chloride ..	grams 360
Hydrochloric acid, sp. gr. 1.20	cc. 216
Water	cc. 4000

After the surface has been pretreated, as above described, the pretreating solution is removed and the surface is thoroughly washed so as to remove the pretreating solution as completely as possible. The surface is then ready for the metallizing operation. This operation consists in sub-

jecting the surface to a silvering bath to precipitate the silver thereon. The silvering bath may comprise a water solution of sodium potassium tartrate and silver nitrate or a water solution of formaldehyde, which is combined with a solution of silver nitrate and ammonia under conditions such that the silver is precipitated from the silver nitrate solution onto the surface of the article.

These solutions are preferably prepared separately and are mixed only when the metallizing operation is to be carried out. The formaldehyde or sodium potassium tartrate serves to reduce the silver and cause the same to be deposited on the surface. The solution should be agitated throughout the metallizing operation.

The details of the operation and the amounts of reducer solution and silver nitrate solution required depend upon the number of articles and their surface area. The following quantities and method are suitable for 1000 small objects, each approximately 1 inch in diameter:

Reducer solution:		
Formaldehyde, 40% solution in water	cc.	22
Silver solution:		
Silver nitrate	grams	33.3
Dissolve in small quantity of distilled water e.g.	cc.	40
Ammonia water, 28%, enough to clear up the solution, about	cc.	28

The articles should be immersed in a suitable quantity of water, e.g. 2 to 4 gallons. The silver nitrate solution is added first, and the articles agitated for 1 to 2 minutes. Then the reducer solution is added, the entire mixture is well shaken, and the solution is then agitated slowly during the silvering operations.

The thickness of the layer of silver thus precipitated will depend, in general, upon the length of time that the silver nitrate solution is in contact with the surface and the concentration of silver in the solution. Preferably, the solution is constantly agitated or caused to flow over the surface so that a fresh part of the solution is always in contact therewith. If, after one treatment of this type, the object is not uniformly coated, the operation may be repeated until a coating of the desired consistency and thickness is built up on the treated surface. The silvered surface may now be polished and it may be suitable for certain ornamental purposes. If desired, however, the silvered surface may be used as a conductor for the electroplating of any desired metal thereon.

For this purpose, the object is placed in the usual electrolyte having a composition depending upon the metal to be deposited and the silvered coating may be used as a cathode onto which the plating metal is applied in the usual manner. The metal coating thus applied will adhere sufficiently to permit buffing and polishing and to produce a finish resembling a metal article.

In the above process, it is to be understood that certain of the steps may be omitted in various instances, depending upon the condition of the material and the type of coating required. For example, if the silvered coating is to be the finished surface, particularly in the case of cast resins and thermoplastic materials, the preliminary depolishing may be omitted. It may also be omitted if only a thin electro-plating is to be added which does not have sufficient tensile strength to be peeled from the surface, or if an extremely heavy electro-plating is to be applied which would have sufficient strength in itself to resist the tendency to peel. Similarly, the preliminary depolishing may be omitted if the plastic material is a matrix for electroforming a thick plate, which is subsequently peeled. For coatings having an intermediate thickness, however, which are sufficiently strong to be peeled from the surface, but are not sufficiently rigid to resist such action, the depolishing has been found to be advantageous.

This process is particularly adapted to ornamentation of plastic materials of the type above referred to inasmuch as it may be applied by means of a stencil. If, for example, the surface is covered by a suitable stencil the steps of pretreating and cleaning the surface, treating with the stannous chloride-hydrochloric acid solution as aforesaid, and depositing the silver thereon from the silver nitrate solution may all be carried out in the presence of the stencil and will deposit the metal in the form of a stencilled design. Thereafter, if a subsequent electroplating is required, the silvered coating will serve to form the base for the electroplating and cause the latter to also assume the predetermined design.

Objects treated in this manner present the appearance of metal, but have a weight corresponding to that of the plastic and also have the advantage that they may be formed or moulded in any desired shape much more readily and inexpensively than a metal article could be so formed and that, when coated, they serve as a substitute for the metal article.

The process is particularly adaptable for novelties, such as costume jewellery, ash trays or ornametal figures.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The method of metallizing the surface of an organic plastic material which includes the pretreatment of the surface of the material for sensitizing said surface pre-

paratory to metallizing, with an aqueous solution of stannous chloride including hydrochloric acid in quantity such that the solution becomes clear and remains clear during said treatment.

2. The method of metallizing the surface of an organic plastic material according to Claim 1, wherein the stannous chloride solution comprises the following ingredients in the proportions specified :

Stannous Chloride	grams. 360
Hydrochloric Acid, sp. gr. 1.20	cc. 216
Water	cc. 4000

3. The method of metallizing the surface of an organic plastic material which comprises treating the surface with the solution of stannous chloride and hydrochloric acid according to Claim 1 or 2 to cause the same to have characteristics suitable for metallizing, washing the surface to remove said solution and applying to said surface a solution of silver nitrate, ammonia and a reducing agent under conditions to precipitate the silver thereon to form a metallic layer.

4. The method of metallizing the surface of a cellulose ester product which comprises treating said surface with a caustic alkali solution to depolish the same, washing the surface to remove said alkali solution, then treating the depolished surface with the solution of stannous chloride and hydrochloric acid according to Claim 1 or 2, to cause the same to have characteristics suitable for metallizing, washing the surface to remove said stannous chloride solution and applying to said surface a solution of silver nitrate, ammonia and a reducing agent under conditions to precipitate the silver thereon to form a metallic layer.

5. Method according to Claim 3 or 4 comprising the step of electrodepositing metal on said layer.

6. Method according to Claim 5, wherein metal is deposited in sufficient thickness to afford tensile strength enabling the metal to be peeled off.

7. An article of manufacture comprising an organic plastic material having an adherent silver layer deposited thereon and firmly adherent thereto, said article being produced in accordance with the process set forth in Claim 3 or 4.

8. An article of manufacture comprising an organic plastic material having an adherent silver layer deposited thereon and firmly adherent thereto and a layer of metal electrolytically deposited on said silver layer, said article being produced in accordance with the process set forth in Claim 5.

9. A method of metallizing organic plastic materials substantially as herein described.

Dated this 16th day of July, 1947,

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Reference has been directed, in pursuance of Section 7, Sub-section (4), of the Patents and Designs Acts, 1907 to 1946, to Specification No. 296,459.

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